

Mott physics in $2p$ electron dioxygenyl magnet : O_2MF_6 ($M=Sb, Pt$)

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We have investigated electronic structures and magnetic properties of O_2MF_6 ($M=Sb, Pt$), which are composed of two building blocks of strongly correlated electrons: O_2^+ dioxygenyls and MF_6^- octahedra, by employing the first-principles electronic structure band method. For O_2SbF_6 , as a reference system of O_2PtF_6 , we have shown that the Coulomb correlation of $O(2p)$ electrons drives the Mott insulating state. For O_2PtF_6 , we have demonstrated that the Mott insulating state is induced by the combined effects of the Coulomb correlation of $O(2p)$ and $Pt(5d)$ electrons and the spin-orbit (SO) interaction of $Pt(5d)$ states. The role of the SO interaction in forming the Mott insulating state of O_2PtF_6 is similar to the case of Sr_2IrO_4 that is a prototype of a SO induced Mott system with $J_{eff} = 1/2$.

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Mott transition in strongly correlated electron systems has been extensively studied for $3d$ transition metal (TM) oxides, in which the degenerate $3d$ states are usually split by the crystal-field (CF) and then the Coulomb correlation effect produces the energy separation between the upper and lower Hubbard bands.[1] The spin-orbital dependent superexchange interaction of Kugel-Khomskii type can be derived based on orbital polarizations of $3d$ states in these Mott insulating states.[2, 3] According to recent experimental and theoretical works, the similar Mott physics is realized in $2p$ electron molecular solids (KO_2)[4–6] and also in $5d$ TM oxides (Sr_2IrO_4)[7–10], which signifies a new paradigm of spin-orbital physics. The bands in $2p$ electron molecular solids are almost molecular-level like due to the weak intermolecular interaction, and so the band width W near the Fermi level E_F is small with respect to on-site Coulomb repulsion U , resulting in the Mott insulating state.[4–6] On the other hand, in $5d$ TM oxides, the large spin-orbit (SO) interaction as much as ~ 0.4 eV[7] brings about the small W by lifting the degeneracy of $5d$ states and also by reducing the hopping strength.[7, 10] In the strong SO interaction limit, electronic structures of $5d$ TM oxides are determined by the relative magnitude between W and U of $5d$ electrons.[8, 9] In this context, dioxygenyl magnet O_2PtF_6 is interesting in that it is a $2p$ electron molecular solid containing $5d$ TM element, which possesses both effects of the strong Coulomb correlation and the strong SO interaction.

O_2MF_6 ($M=Sb, Pt$) were reported to be insulators.[11–13] O_2MF_6 is composed of O_2^+ dioxygenyls and MF_6^- octahedra, as depicted in Fig. 1. Dioxygenyl O_2^+ ion has the electronic configuration of $\sigma_g^2\pi_u^4\pi_g^{*1}$ (see Fig. 2(a)). Hence the localized magnetic moment would be generated from one unpaired electron on the degenerate π_g^* orbital. Magnetic susceptibility data showed the Curie-Weiss behaviors with low Curie temperatures, $T_C = 0.8$ K for O_2SbF_6 and $T_C = 4$ K for O_2PtF_6 , respectively, which implies the rather weak superex-

change interaction between localized magnetic moments. Electron spin resonance (ESR) experiment also revealed the existence of the localized magnetic moment of O_2^+ in O_2SbF_6 and the ferrimagnetic ordering between the magnetic moments of O_2^+ and Pt in O_2PtF_6 . [12]

Local electronic structure of O_2^+ in Fig. 2 is similar to that of O_2^- in KO_2 superoxide that has one hole (three electrons) in the π_g^* state. Electronic structure calculations for various superoxides (KO_2 , RbO_2 , Rb_4O_6) indicated that the conventional local density approximation (LDA) or the generalized gradient approximation (GGA) underestimates the Coulomb correlation interaction of open shell $2p$ electrons in superoxides. Only after the inclusion of on-site Coulomb repulsion U in the LDA+ U or GGA+ U schemes, the insulating nature of superoxides was properly described.[4, 5, 14–18]

We have investigated electronic structures and magnetic properties of O_2PtF_6 by employing the first-principles band structure calculation incorporating both

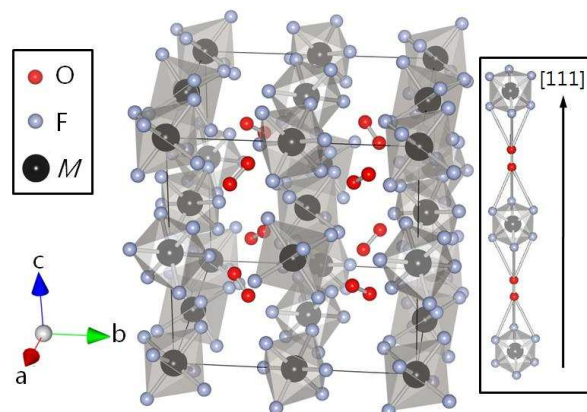


FIG. 1: (Color online) Crystal structure of O_2MF_6 ($M=Sb, Pt$) composed of O_2^+ dioxygenyls and MF_6^- octahedra. There are eight O_2^+ and MF_6^- ions in a unit cell. In the right, the molecular configuration of O_2^+ and MF_6^- along the $[111]$ direction is shown.

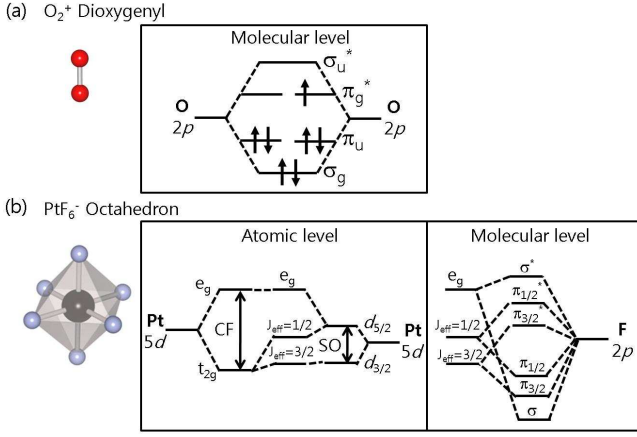


FIG. 2: (Color online) (a) Molecular level of O_2^+ dioxygenyl ion. (b) Schematic local electronic structure of PtF_6^- ion. Pt($5d$) atomic states are split into e_g and $J_{eff} = 1/2, 3/2$ under the octahedral crystal field (CF) with the spin-orbit (SO) interaction. Then Pt($5d$)-F($2p$) hybridization splits those levels into bonding and antibonding molecular states with π and σ channels.

the Coulomb correlation and the SO effect. As a reference system, we have also examined electronic structures of O_2SbF_6 . For O_2SbF_6 , we have confirmed that the Coulomb correlation of O($2p$) electrons yields the Mott insulating state, consistently with experiments. For O_2PtF_6 , we have shown that not only correlation effects of both O($2p$) and Pt($5d$) electrons but also the strong SO interaction of the $5d$ states are essential to describe its Mott insulating state.

We have performed electronic structure calculations for the experimental unit cell of O_2MF_6 ($M=Sb, Pt$) with bcc structure of $Ia_3(206)$ space group.[19] We have employed the full-potential augmented plane wave (FLAPW) band method[20] implemented in WIEN2k package.[21] We have considered the on-site U of both O($2p$) and Pt($5d$) electrons in the GGA+ U [22] and the SO interaction effect is included as a second variational procedure in the GGA+SO and the GGA+SO+ U scheme. The spin direction has chosen to be (001) direction for the consideration of SO interaction. For results below, U value was chosen to be 10 eV for both O($2p$) and Pt($5d$) states.[23, 24] We have assumed the ferromagnetic state for O_2SbF_6 , and the ferrimagnetic ordering between the magnetic moments of O_2^+ and Pt for O_2PtF_6 . [25] To allow the orbital polarization of π_g^* states, as was realized in KO_2 superoxide,[5] we have removed all the symmetry operators except inversion symmetry.

Figure 3 shows the calculated density of states (DOS) of O_2SbF_6 both in the GGA and GGA+SO+ U schemes. Most valence electrons of Sb are transferred into F, and $4d^{10}$ occupied states of Sb^{5+} are located ~ 25 eV below E_F . Hence only a small amount of Sb states originating from the hybridization with F($2p$) states exists near E_F .

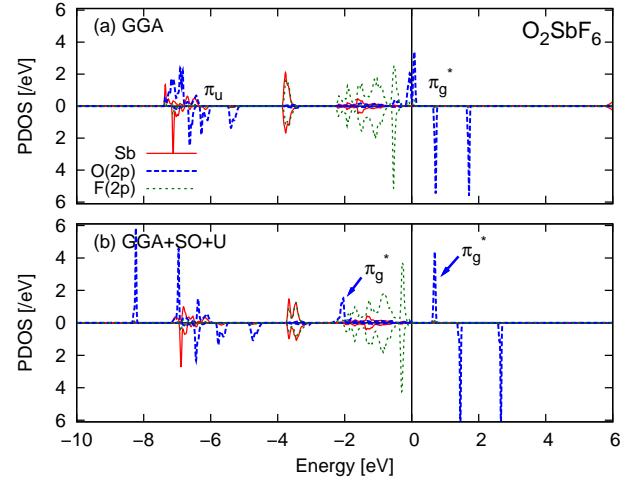


FIG. 3: (Color online) (a) Partial density of states (PDOS) of O_2SbF_6 in the GGA. The red solid, blue dashed, and green dotted lines denote DOS of Sb, O($2p$), and F($2p$) states, respectively. (b) PDOS in the GGA+SO+ U . The inclusion of Coulomb correlation yields the separation of π_g^* band into the occupied lower Hubbard and unoccupied upper Hubbard bands, as indicated by blue arrows. U value was chosen to be 10 eV for O($2p$).

Therefore, O_2SbF_6 is a typical O($2p$) molecular solid like KO_2 . The GGA in Fig. 3(a) yields the metallic state for O_2SbF_6 with π_g^* spin \uparrow states being located at E_F . On the other hand, the GGA+SO+ U in Fig. 3(b) considering the correlation effect of O($2p$) electrons yields the correct insulating state by separating the π_g^* states into occupied (lower Hubbard) and unoccupied (upper Hubbard) states with a gap of $\Delta_H = 2.55$ eV. We have also found that electronic structures in the GGA+ U are almost the same as those in the GGA+SO+ U , implying that the role of the SO interaction in O_2SbF_6 is minor. Note that, in KO_2 superoxide, the degenerate π_g^* states tend to be split by coherent tilting of the O_2^- molecular axes. This mechanism is called "magnetogyration", which invokes the structural and magnetic transitions concomitantly.[26] Likewise, the degeneracy of the π_g^* states in O_2SbF_6 is lifted by trigonal CF coming from neighboring F^- ions.[11, 12]. This feature is revealed in the spin-density (SD) plot in Fig. 5(a), which manifests the directionally polarized π_g^* orbital shape at each O_2^+ site.

There was controversy on the existence of SO effects in the π_g^* states of O_2MF_6 . In one group,[11, 27] g_{eff} factor determined from the magnetic susceptibility and ESR was close to 2 independently of the direction of magnetic field, which reflects the negligible SO effect, while, in another,[12] g_{eff} was reduced a lot along the molecular axis (1.73), which reflects the large orbital moment along that molecular axis. In the present GGA+SO+ U calculation, the orbital magnetic moment is indeed induced along the molecular axis of O_2^+ . However, its magnitude,

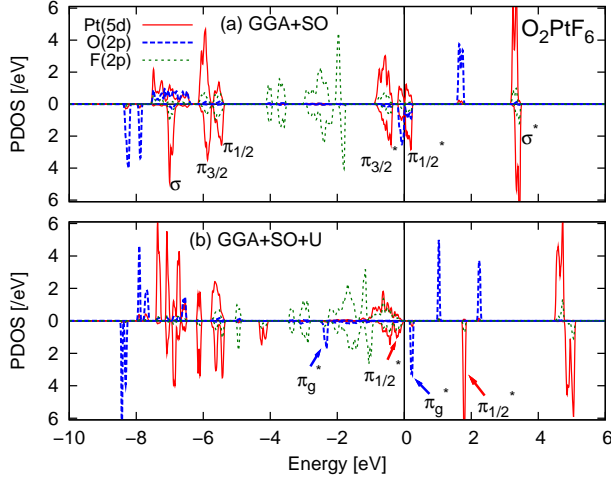


FIG. 4: (Color online) (a) PDOS of O_2PtF_6 in the GGA+SO. The red solid, blue dashed, and green dotted lines denote DOS of Pt(5d), O(2p), and F(2p) states, respectively. (b) In GGA+SO+U, inclusion of the Coulomb correlation and the SO interaction yields the separation of (i) π_g^* states of O(2p), as indicated by blue arrows, and (ii) $\pi_{1/2}^*$ states of Pt(5d), as indicated by red arrows. U values were chosen to be 10 eV for both O(2p) and Pt(5d).

$0.02 \mu_B$ per each O_2^+ , is only $\sim 2\%$ of the spin magnetic moment ($1.00 \mu_B$), which is too small to produce reduced g factor as reported by Ref.[12]. This result implies that the SO interaction is suppressed in O_2SbF_6 due to the quenched orbital moment of O_2^+ , similarly to the case of low symmetry structure of KO_2 . [5, 18]

Figure 4 shows the calculated DOS of O_2PtF_6 . Noteworthy is that Mott insulating state is obtained only in the GGA+SO+U (Fig. 4(b)), in which both the Coulomb correlations of O(2p) and Pt(5d) electrons and the SO interaction are considered. Namely, the GGA, GGA+SO, and GGA+U schemes without including the SO interaction do not give correct insulating state of O_2PtF_6 . Local electronic structure of Pt^{5+} in O_2PtF_6 is close to that of Ir^{4+} in Sr_2IrO_4 . Both Pt^{5+} and Ir^{4+} have $5d^5$ electronic configuration under the octahedral CF with strong SO interaction (see Fig. 2(b)). Since the CF is stronger than the Hund exchange interaction, they both have the low-spin (LS) states. As shown in Fig.2(b), the SO interaction splits t_{2g} states of Pt into $J_{eff} = 1/2, 3/2$, which then hybridize with F(2p) states to produce $\pi_{1/2}^*$ states at E_F (see Fig. 4(a)). Due to the shorter Pt-F bond length ($\sim 1.88 \text{ \AA}$) [19] than that of Ir-O ($\sim 2.00 \text{ \AA}$), [28] the bands in O_2PtF_6 are almost molecular-level like. In the GGA+SO in Fig. 4(a), the SO split $\pi_{1/2}^*$ states are still degenerate to make O_2PtF_6 metallic. The degenerate $\pi_{1/2}^*$ states become split only after the inclusion of Coulomb interaction of Pt(5d) electrons, as shown in Fig.4(b). Note that the $\pi_{1/2}^*$ states are not to be split in the GGA+U even with very large U value, unless the SO interaction is included.

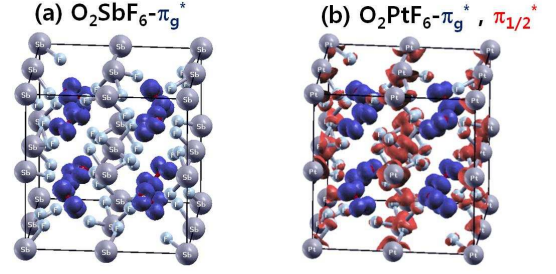


FIG. 5: (Color online) (a) SD plot of O_2SbF_6 in the GGA+SO+U. Directionally polarized π_g^* orbitals in blue are manifested. (b) SD plot of O_2PtF_6 in the GGA+SO+U. The directionally polarized π_g^* orbitals in blue and the directionally non-polarized $\pi_{1/2}^*$ orbitals in red are manifested.

In general, ions with t_{2g}^5 occupation in the LS state are Jahn-Teller (JT) active. It was once reported that reduced g_{eff} factor ($g = 1.86$) for the LS state ($S = 1/2$) of Pt^{5+} in O_2PtF_6 could be explained by the JT effect.[12] The JT distortion, however, has not been detected in O_2PtF_6 . The neutron diffraction[29] provided that PtF_6^- has a regular octahedron structure. No anomaly in the temperature dependent magnetic susceptibility[12] for O_2PtF_6 also indicates the absence of structural phase transition. Electronic structures in Fig. 4 really verify that the degeneracy of t_{2g} states is lifted by the SO effect not by the JT effect. The orbital magnetic moment of Pt ion is as much as $0.52 \mu_B$, which is comparable to the spin magnetic moment of $0.60 \mu_B$. Thus, it is this large orbital magnetic moment of Pt that is responsible for the deviation of the observed g_{eff} factor from two. Indeed, the feature of the lifted degeneracy is revealed in the SD plot in Fig. 5(b), which manifests the directionally non-polarized $\pi_{1/2}^*$ orbital shape at each Pt^{5+} site, in contrast to the directionally polarized π_g^* orbital shape at each O_2^+ site.

Note, in Fig. 4(a), that there exists substantial hybridization effect between Pt(5d)-O(2p) states, even though Pt and O are not nearest neighbors (see Fig.1). In the case of Sr_2IrO_4 , the SO interaction not only splits degenerate t_{2g} states but also reduces the hybridization with neighboring O(2p) states because of its directionally non-polarized symmetric nature.[7] Similarly, in O_2PtF_6 , Pt(5d)-O(2p) hybridization seems to be reduced a lot by considering the SO interaction. Band structures in Fig.6 confirm this phenomenon. The blue (red) dot denotes the amount of O(2p) (Pt(5d)) component in the wave function. As shown in Fig.6(a) and (d), without inclusion of the SO interaction (GGA and GGA+U), bands near E_F are more dispersive. In contrast, inclusion of the SO interaction in the GGA+SO and GGA+SO+U reduces (i) the band dispersion, (ii) the overlap between O(2p)-Pt(5d) states, and (iii) the direction dependence of O(2p) and Pt(5d) components, as clearly seen in Fig.6(b)

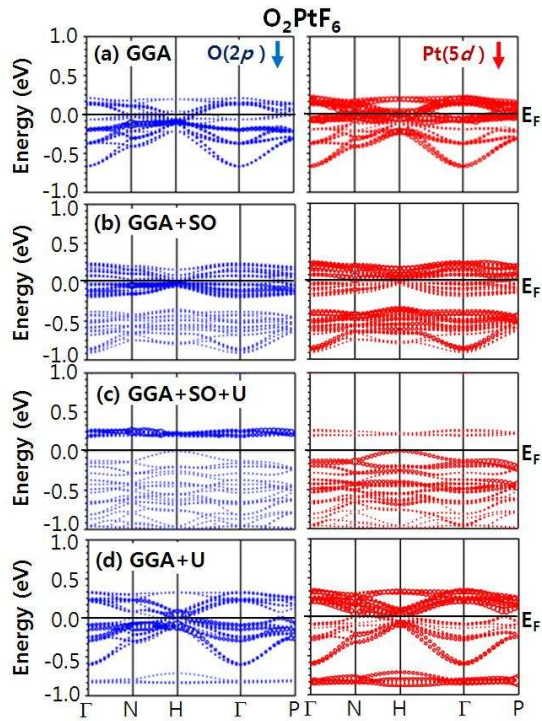


FIG. 6: (Color online) (a) Spin \downarrow band structures of O_2PtF_6 in the GGA. The size of blue (red) dot denotes the amount of $\text{O}(2p)$ ($\text{Pt}(5d)$) component in the wave function. (b) The same as (a) in the GGA+SO. (c) The same as (a) in the GGA+SO+ U . (d) The same as (a) in the GGA+ U .

and (c). The SO split $\pi_{1/2}^*$ state in Fig.6(b) has a narrow band width of $W=0.44$ eV, which is much smaller than that of the original antibonding π states ($W=0.84$ eV) in Fig.6(a). Therefore, the SO interaction plays an important role in realizing the Mott insulating state of O_2PtF_6 , as in the case of Sr_2IrO_4 .

In conclusion, we have demonstrated that dioxygenyl magnet O_2PtF_6 is the first $2p$ electron Mott insulator induced by combined effects of the Coulomb correlation and the SO interaction. For O_2SbF_6 , a typical $2p$ molecular solid, we have shown that the Coulomb correlation of $\text{O}(2p)$ electrons drives the Mott insulating state. The SO interaction in dioxygenyl O_2^+ in O_2SbF_6 is suppressed by the strong CF of neighboring F^- ions, as was corroborated by the quenched orbital moment of O_2^+ . For O_2PtF_6 , the Mott insulating state is obtained by considering both the Coulomb correlation of $\text{O}(2p)$ and $\text{Pt}(5d)$ electrons and the SO interaction of $\text{Pt}(5d)$ states. The role of the SO interaction in O_2PtF_6 is similar to the case of Sr_2IrO_4 , which implies that O_2PtF_6 is also a typical SO induced Mott system with $J_{\text{eff}} = 1/2$. The proposed aspects of strong SO interaction in O_2PtF_6 remain to be confirmed by further experiments: (i) large orbital moment of Pt ion, (ii) absence of the JT distortion of PtF_6 octahedron at low temperature.

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 - [23] We have checked that electronic structures are consistent for U values of 7 – 12 eV. Employed U value of 10 eV corresponds to the Coulomb interaction of $2p$ electrons in O atoms or $5d$ electrons in Pt atoms. Such large U value would be screened by the intramolecular hybridization in O_2^+ or PtF_6^- , [4, 24] as displayed in the smaller energy separation between occupied and unoccupied states of $\text{O}(2p)$

- ($\Delta_H = 2.55$ eV) or Pt(5d) ($\Delta_H = 1.70$ eV) in Fig.4(b). The screening by the intramolecular hybridization has also been confirmed in Ref.[6] for KO_2 .
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